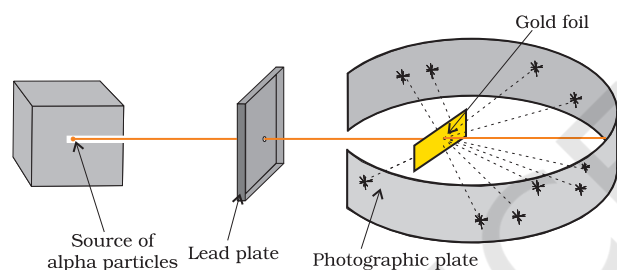


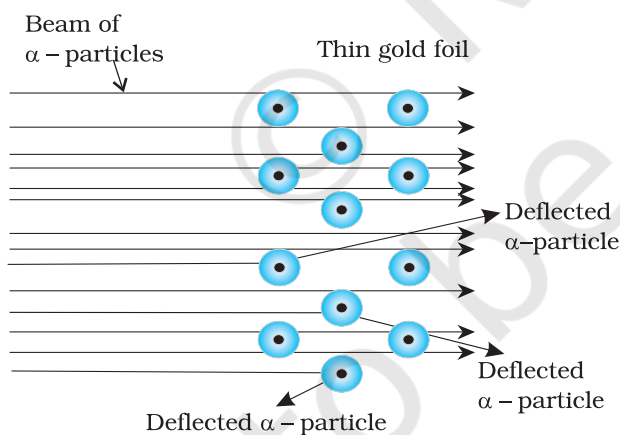
nuclei as when α -particles combined with two electrons yielded helium gas. β -rays are negatively charged particles similar to electrons. The γ -rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α -particles are the least, followed by β -rays (100 times that of α -particles) and γ -rays (1000 times of that α -particles).

2.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α -particles. Rutherford's famous **α -particle scattering experiment** is



A. Rutherford's scattering experiment



B. Schematic molecular view of the gold foil

Fig. 2.5 Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected.

represented in Fig. 2.5. A stream of high energy α -particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α -particles struck the screen, a tiny flash of light was produced at that point.

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α -particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that:

- (i) most of the α -particles passed through the gold foil undeflected.
- (ii) a small fraction of the α -particles was deflected by small angles.
- (iii) a very few α -particles (~ 1 in 20,000) bounced back, that is, were deflected by nearly 180° .

On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom:

- (i) Most of the space in the atom is empty as most of the α -particles passed through the foil undeflected.
- (ii) A few positively charged α -particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α -particles.
- (iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if

Problem 2.1

Calculate the number of protons, neutrons and electrons in ${}^{80}_{35}\text{Br}$.

Solution

In this case, ${}^{80}_{35}\text{Br}$, $Z = 35$, $A = 80$, species is neutral

Number of protons = number of electrons
= $Z = 35$

Number of neutrons = $80 - 35 = 45$,
(equation 2.4)

Problem 2.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons
= $16 + 16 = 32$

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = $18 - 16 = 2$.
Symbol is ${}^{32}_{16}\text{S}^{2-}$.

Note : Before using the notation ${}^A_Z\text{X}$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by $A - Z$, whether the species is neutral or ion.

2.2.5 Drawbacks of Rutherford Model

As you have learnt above, Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the

massive sun and the electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets is given by the expression

$$\left(G \cdot \frac{m_1 m_2}{r^2} \right) \text{ where } m_1 \text{ and } m_2 \text{ are the masses, } r$$

is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements.

The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary

* Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.

around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom.

Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

2.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

- (i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and
- (ii) Experimental results regarding atomic spectra.

First, we will discuss about the dual nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4.

2.3.1 Wave Nature of Electromagnetic Radiation

In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occurred in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed

in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations.

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called **electromagnetic waves** or **electromagnetic radiation**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscles). It was only in the 19th century when wave nature of light was established.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6).

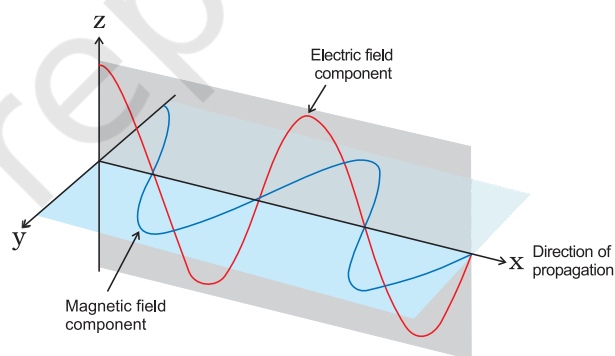


Fig.2.6 The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.

Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

- (i) The oscillating electric and magnetic fields produced by oscillating charged particles

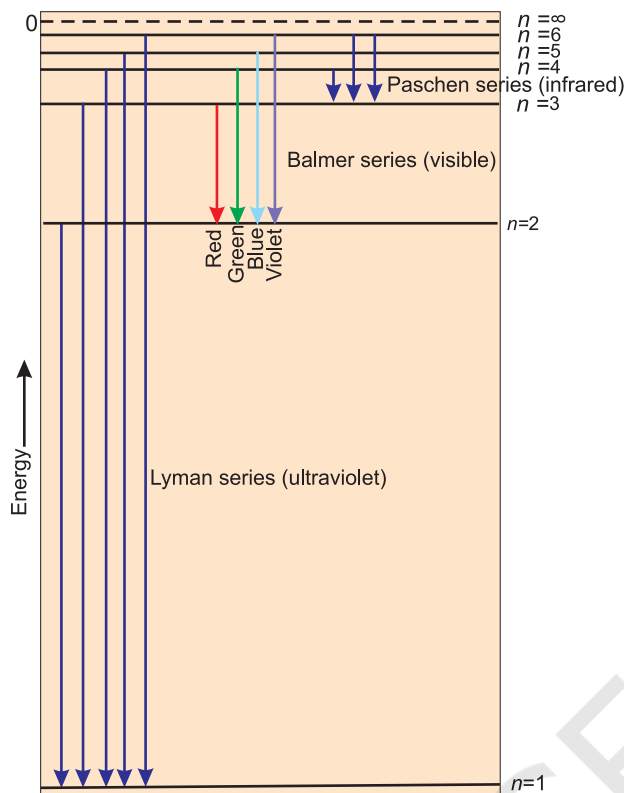


Fig. 2.11 Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)

more and more complex for heavier atom. There are, however, certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

2.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to

rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

- i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
- ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner.

Angular Momentum

Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e , moving in a circular path of radius r around the nucleus,

$$\text{angular momentum} = I \times \omega$$

Since $I = m_e r^2$, and $\omega = v/r$ where v is the linear velocity,

$$\therefore \text{angular momentum} = m_e r^2 \times v/r = m_e v r$$

- iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by:

$$v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \quad (2.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

- iv) The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11)

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots \quad (2.11)$$

Where m_e is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving.

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. That means angular momentum is quantised. Radiation is emitted or absorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

- The stationary states for electron are numbered $n = 1, 2, 3, \dots$. These integral numbers (Section 2.6.2) are known as **Principal quantum numbers**.
- The radii of the stationary states are expressed as:

$$r_n = n^2 a_0 \quad (2.12)$$
 where $a_0 = 52.9$ pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is $n=1$). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.
- The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -R_H \left(\frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots \quad (2.13)$$

where R_H is called **Rydberg constant** and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is

$$E_1 = -2.18 \times 10^{-18} \left(\frac{1}{1^2} \right) = -2.18 \times 10^{-18} \text{ J.}$$

The energy of the stationary state for $n = 2$, will

$$\text{be : } E_2 = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} \right) = -0.545 \times 10^{-18} \text{ J.}$$



**Niels Bohr
(1885–1962)**

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J.

Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number $= n = \infty$ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (2.13) so that $E_\infty = 0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by $n=1$ which corresponds to the most stable orbit. We call this the ground state.

and its energy is lowered. That is the reason for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and $n = \infty$.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ , Li^{2+} , Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{J} \quad (2.14)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{pm} \quad (2.15)$$

where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z . This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

2.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$$\Delta E = E_f - E_i \quad (2.16)$$

Combining equations (2.13) and (2.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2} \right) - \left(-\frac{R_H}{n_i^2} \right) \quad (\text{where } n_i \text{ and } n_f$$

stand for initial orbit and final orbits)

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \text{J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.17)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\begin{aligned} \nu &= \frac{\Delta E}{h} = \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{2.18 \times 10^{-18} \text{J}}{6.626 \times 10^{-34} \text{Js}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned} \quad (2.18)$$

$$= 3.29 \times 10^{15} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{Hz} \quad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.20)$$

$$\begin{aligned} &= \frac{3.29 \times 10^{15} \text{s}^{-1}}{3 \times 10^8 \text{m s}^{-1}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{m}^{-1} \end{aligned} \quad (2.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, ΔE is negative and energy is released.

The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 2.10

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_1 = 5$ and $n_2 = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (2.17)

$$\begin{aligned}\Delta E &= 2.18 \times 10^{-18} \text{ J} \left[\frac{1}{5^2} - \frac{1}{2^2} \right] \\ &= -4.58 \times 10^{-19} \text{ J}\end{aligned}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\begin{aligned}v &= \frac{\Delta E}{h} \\ &= \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \\ &= 6.91 \times 10^{14} \text{ Hz}\end{aligned}$$

$$\lambda = \frac{c}{v} = \frac{3.0 \times 10^8 \text{ m s}^{-1}}{6.91 \times 10^{14} \text{ Hz}} = 434 \text{ nm}$$

Problem 2.11

Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 10^{-18} \text{ J})Z^2}{n^2} \text{ atom}^{-1}$$

For He^+ , $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} \text{ J})(2^2)}{1^2} = -8.72 \times 10^{-18} \text{ J}$$

The radius of the orbit is given by equation (2.15)

$$r_n = \frac{(0.0529 \text{ nm})n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529 \text{ nm})1^2}{2} = 0.02645 \text{ nm}$$

2.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+ , Li^{2+} , Be^{3+} , and so on). However, Bohr's model was too simple to account for the following points.

- It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).
- It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

2.5 TOWARDS QUANTUM MECHANICAL MODEL OF THE ATOM

In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were :

- Dual behaviour of matter,
- Heisenberg uncertainty principle.

2.5.1 Dual Behaviour of Matter

The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle.